

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開2002-50351

(P2002-50351A)

(43) 公開日 平成14年2月15日 (2002.2.15)

(51) IntCl. ⁷	識別記号	F I	テームト [*] (参考)
H 0 1 M 4/38		H 0 1 M 4/38	A 5 H 0 5 0
C 2 2 C 1/00		C 2 2 C 1/00	N

審査請求 未請求 請求項の数2 O L (全 3 頁)

(21) 出願番号 特願2000-236332(P2000-236332)

(22) 出願日 平成12年8月4日 (2000.8.4)

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Fターム(参考) 5H050 AA15 AA19 BA14 CB17 GA02

GA10

(54) 【発明の名称】 電池用水素吸蔵合金の製造方法

(57) 【要約】

【課題】 溶解中のマグネシウムの蒸発を抑制し、所定量のマグネシウムを合金内に含有させ、真空溶解、又は雰囲気溶解後に炉内を大気に解放するときの安全を確保する方法を提供する。

【解決手段】 Mgを添加するための原料として融点が650℃以上のMg金属、又はMg合金を使用することを特徴し、さらに、Ni、Co等の高融点金属を溶解した後添加することを特徴とする。

【特許請求の範囲】

【請求項1】 Mgを添加する希土類系水素吸蔵合金の製造方法であって、該Mgの添加原料として融点が650℃以上であるMg合金、又はMg金属を使用することを特徴とする水素吸蔵合金の製造方法。

【請求項2】 上記希土類系水素吸蔵合金がNi及び／又はCoを含み、上記Mgの添加原料を溶解時に添加する場合、少なくとも該Ni及び／又はCoの高融点金属を溶解した後、溶湯内に添加する請求項1に記載の水素吸蔵合金の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、水素吸蔵合金の製造方法に関し、特に、ニッケル水素二次電池に用いられる負極用の水素吸蔵合金の製造方法に関するものである。

【0002】

【従来の技術】ニッケル水素二次電池において、負極に用いられる水素吸蔵合金の溶解方法として従来から高周波溶解方法、アーク溶解法等が用いられてきている。また、原料は、La、Ce、Pr、Nd、Sm等の希土類金属や、それらの混合物であるミッシュメタル（以下、「Mm」という。）とニッケル、コバルト、マンガン、アルミニウムの金属を使用してきた。最近、これらの金属以外にマグネシウムを合金中に0.5重量％程度含有させることにより微粉化が抑制されたり、水素吸蔵含量が増大したりすることがわかってきた。従来のMm等にもMgが不純物として含まれているが、溶解中に蒸発し、ほとんどできあがった合金中に残存していない。その理由としては、マグネシウムの飽和蒸気圧が他の金属に比べ高いことと希土類とMgとの合金は融点が低くなるため、溶解が早くなり、結果的に溶湯に在る時間が長くなり、溶解中に蒸発してしまうことがわかっている。蒸発したマグネシウムは、溶解炉壁に付着し、溶解、鑄込み後、雰囲気置換チャンバーを大気に解放したとき、燃焼、又は爆発の可能性があり非常に危険である。

【0003】

【発明が解決しようとする課題】本発明は、これら従来技術の課題を解決するもので、溶解中のマグネシウムの蒸発を抑制し、所定量のマグネシウムを合金内に含有させ、真空溶解、又は雰囲気溶解後に炉内を大気に解放するときの安全を確保する方法を提供するものである。

【0004】

【課題を解決するための手段】本発明は、Mgを添加するための原料として融点が650℃以上のMg金属、又はMg合金を使用することに特徴をもち、さらに、Ni、Co等の高融点金属を溶解した後に添加することを特徴とする。そこで、Mgの添加原料は、融点を650℃以上にした合金、又はマグネシウムメタルを添加する場合、NiやCo等の高融点金属が溶融した後に添加す

ることにより、マグネシウムの含有された金属が溶湯として存在している時間が短くなり、溶湯から蒸発するMg量が抑制される効果が期待される。結果として、炉壁等へのMgの付着量が減少し、炉内を大気解放時により安全に作業を進めることができるようになり、さらに、できあがった合金中のマグネシウム含有量を高くすることができる。

【0005】

【発明の実施の形態】本発明の対象となる水素吸蔵合金は、LaNi₅、MmNi₅、LmNi₅（LmはLaリッチなミッシュメタルを表す。）系合金であることを特徴としており、Niの一部を、Co、Al、Mnで置換してもよい。

【0006】本発明の水素吸蔵合金製造方法は、以下のように行う。所定量の各元素を秤量し、高周波溶解炉にてArガス等の不活性ガス（0.02～0.2MPa）で溶解する。この溶解原料としてMg金属や融点650℃以上の合金を用いる。例えば、MgNi₅等が挙げられる。添加量としては、用いる水素吸蔵合金に対し、0.05～2.0重量％、好ましくは0.1～1.0重量％とする。本発明の方法は、希土類系水素吸蔵合金がNi及び／又はCoを含み、Mgの添加原料を溶解時に添加する場合、少なくともNi及び／又はCoの高融点金属を溶解した後、溶湯内に添加することを特徴とする。例えば、溶解の際、初期の坩堝内には、所定量秤量したNi、Co、Mn、Alをいれて溶解をはじめ。それらが溶解した後、La、Ce、Pr、Nd、又はMmの秤量品と同時にMg金属、又はMg合金を溶湯内に添加する。このとき、一旦、溶湯温度が低下するので再び所定温度まで上昇するのを待って、鑄型、又はテーブル上に傾注し、冷却する。

【0007】本発明の製造法で得られた合金は、既知の方法で、熱処理、粉碎し、電極用水素吸蔵合金とする。例えば、Arガス等の不活性雰囲気下（0.08～0.2MPa）で800～1200℃で5～20時間熱処理を行い、その後、Ar等の不活性雰囲気下で衝撃式又は摩砕式粉碎機又はジェットミルなどの粉碎機にて平均粒径4～70μmになるように粉碎して本発明の水素吸蔵合金を得ることができる。

【0008】

【実施例】以下、実施例によって本発明を詳述するが、本発明はこれに限定されるものではない。

実施例1、比較例1

下記組成式（1）に示される合金に、該合金に対してMgを0.28重量％添加した合金を作製するのに、合金溶解時に、まず、Ni、Co、Mn、Alを溶解し、その後、Mmと同時にMgメタルを添加する水素吸蔵合金の製造方法を実施例1とし、MgをMm、Ni、Co、Mn、Alと同時に添加し、初期から溶解した場合を、比較例1とした。溶解時のMg添加量に対する合金中の

Mg量を残存率として、表1に示した。溶解は高周波溶解炉、アルゴンガス(0.034MPa)を用い、温度は1340~1420℃であった。

*Mmとしては、La80重量%、Ce12重量%、Pr4重量%、Nd4重量%の組成を用いた。

【0009】

MmNi_{4.17}Co_{0.4}Mn_{0.38}Al_{0.10}

(1)

*

【表1】

	Mgの添加方法	合金中のMg量(重量%)	残存率(%)
実施例1	Ni,Co溶解後にMg金属をMmと同時に添加	0.26	93
比較例1	Ni,Co溶解と同時にMg金属を溶解	0.20	71

【0010】実施例2、比較例2

※し、実施例1の場合と同じようにMgの残存率を表2に

実施例1に示した製造方法にて、添加するMgをNiと10示した。

合金化し、融点を高くした(1100℃)合金を添加する

【0011】

方法を実施例2とし、MgとAlとの合金にて融点を

【表2】

低くした(550℃)合金を添加する方法を比較例2と※

	Mgの添加方法	合金中のMg量(重量%)	残存率(%)
実施例2	融点1100℃のMg-Ni合金を添加	0.27	96
比較例2	融点550℃のMg-Al合金を添加	0.21	75

【0012】表1、表2からわかるとおり、Ni、Co等を溶解後にMgを添加し、また、融点がMg金属(659℃)以上であるほうが合金内により多く残存し、合金外への放散が抑制され、溶解作業時に炉内を大気に解放してもより安全に作業することが可能となることがわかる。

【0013】

【発明の効果】本発明の水素吸蔵合金の製造方法により合金中のMg含有量を所定のものにし、溶解時の蒸発を抑制することにより、より安全な水素吸蔵合金の製造ができる。

CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of Mg alloy whose melting point it is the manufacture approach of the rare earth system hydrogen storing metal alloy which adds Mg, and is 650 degrees C or more as an addition raw material of this Mg, or the hydrogen storing metal alloy characterized by using Mg metal.

[Claim 2] The manufacture approach of the hydrogen storing metal alloy according to claim 1 added in a molten metal after dissolving the refractory metal of this nickel and/or Co at least, when the above-mentioned rare earth system hydrogen storing metal alloy adds the addition raw material of Above Mg including nickel and/or Co at the time of the dissolution.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the manufacture approach of the hydrogen storing metal alloy for negative electrodes used for a nickel hydrogen rechargeable battery about the manufacture approach of a hydrogen storing metal alloy.

[0002]

[Description of the Prior Art] In a nickel hydrogen rechargeable battery, the RF dissolution approach, the arc solution process, etc. have been used from the former as the dissolution approach of the hydrogen storing metal alloy used for a negative electrode. Moreover, rare earth metals, such as La, Ce, Pr, Nd, and Sm, and the metal of the misch metal (henceforth "Mm") which are those mixture, nickel, cobalt, manganese, and aluminum have been used for a raw material. By making magnesium contain about 0.5% of the weight in an alloy recently in addition to these metals has shown that pulverization is controlled or a hydrogen absorption total amount increases. Although Mg is contained in the conventional Mm etc. as an impurity, it evaporates during the dissolution and hardly remains in the alloy which went up by the ability doing. Since the melting point becomes low [the alloy of high things and rare earth, and Mg] as the reason compared with the metal of others [maximum vapor

tension / of magnesium], it turns out that the dissolution becomes early, and the time amount which is in a molten metal as a result becomes long, and it evaporates during the dissolution. When an ambient atmosphere permutation chamber is released to atmospheric air after the dissolution and casting by adhering to a fusion furnace wall, the magnesium which evaporated has the possibility of combustion or explosion, and is very dangerous.

[0003]

[Problem(s) to be Solved by the Invention] This invention solves the technical problem of these conventional technique, controls evaporation of the magnesium under dissolution, makes the magnesium of the specified quantity contain in an alloy, and offers the approach of securing the insurance when releasing the inside of a furnace to atmospheric air after vacuum melting or the ambient atmosphere dissolution.

[0004]

[Means for Solving the Problem] This invention is characterized by adding, after having the description in the melting point using Mg metal or Mg alloy 650 degrees C or more as a raw material for adding Mg and dissolving refractory metals, such as nickel and Co, further. Then, when the addition raw material of Mg adds the alloy which made the melting point 650 degrees C or more, or magnesium metal, the effectiveness that the amount of Mg in which the time amount in which the metal which magnesium contained exists as a molten metal evaporates from a molten metal by becoming short is controlled is expected by adding, after refractory metals, such as nickel and Co, fuse. As a result, the coating weight of Mg to a furnace wall etc. can decrease, and the magnesium content in the alloy which can advance an activity now to insurance by the time of atmospheric-air release, and was further done in the inside of a furnace can be made high.

[0005]

[Embodiment of the Invention] the hydrogen storing metal alloy set as the object of this invention is characterized by being LaNi₅, MmNi₅, and a LmNi₅ (Lm — La — rich misch metal being expressed.) system alloy, and may permute some nickel from Co, aluminum, and Mn.

[0006] As the hydrogen storing metal alloy manufacture approach of this invention is the following, it is performed. Weighing capacity of each element of the specified quantity is carried out, and it dissolves with inert gas (0.02-0.2MPa), such as Ar gas, in a RF fusion furnace. Mg metal and an alloy with a melting point of 650 degrees C or more are used as this dissolution raw material. For example, MgNi₂ grade is mentioned.

It is good to consider as 0.1 – 1.0 % of the weight preferably 0.05 to 2.0% of the weight as an addition to the hydrogen storing metal alloy to be used. When a rare earth system hydrogen storing metal alloy adds the addition raw material of Mg including nickel and/or Co at the time of the dissolution, after the approach of this invention dissolves the refractory metal of nickel and/or Co at least, it is characterized by adding in a molten metal. For example, in the case of the dissolution, in early crucible, nickel, Co, Mn, and aluminum which carried out specified quantity weighing capacity are put in, and the dissolution is begun. After they dissolve, Mg metal or Mg alloy is added in a molten metal to the weighing capacity article and coincidence of La, Ce, Pr, Nd, or Mm. At this time, since molten metal temperature falls, it waits to go up to predetermined temperature again, and it is devoted on mold or a table and it once cools.

[0007] The alloy obtained by the manufacturing method of this invention is a known approach, and it is heat-treated and ground and let it be a hydrogen storing metal alloy for electrodes. For example, heat treatment can be performed at 800–1200 degrees C under inert atmospheres, such as Ar gas, (0.08–0.2MPa) for 5 to 20 hours, it can grind so that it may become the mean particle diameter of 4–70 micrometers under inert atmospheres, such as Ar, after that with an impact type, a grinding type grinder, or grinders, such as a jet mill, and the hydrogen storing metal alloy of this invention can be obtained.

[0008]

[Example] Hereafter, although this invention is explained in full detail according to an example, this invention is not limited to this.

Although the alloy which added Mg 0.28% of the weight to this alloy into the alloy shown in an example 1 and the example of comparison 1 following empirical formula (1) is produced At the time of the alloy dissolution, first, nickel, Co, Mn, and aluminum were dissolved, the manufacture approach of the hydrogen storing metal alloy which adds Mg metal at Mm and coincidence was made into the example 1 after that, Mg was added to Mm, nickel, Co, Mn, aluminum, and coincidence, and the case where it dissolved from the first stage was made into the example 1 of a comparison. It was shown in Table 1, having used the amount of Mg in the alloy to Mg addition at the time of the dissolution as the survival rate. Temperature of the dissolution was 1340–1420 degrees C using a RF fusion furnace and argon gas (0.034MPa).

$\text{MmNi}_{4.17}\text{Co}_{0.4}\text{Mn}_{0.38}\text{Al}_{0.30}$ (1)

As Mm, the presentation of 80 % of the weight of La(s), 12 % of the weight of Ce(s), 4 % of the weight of Pr, and 4 % of the weight of Nd(s) was used.

[0009]

[Table 1]

No translation

[0010] Mg added by the manufacture approach shown in the example 2 and example of comparison 2 example 1 was alloyed with nickel, the approach of adding the alloy (1100 degrees C) which made the melting point high was made into the example 2, the approach of adding the alloy (550 degrees C) which made the melting point low was made into the example 2 of a comparison with the alloy of Mg and aluminum, and the survival rate of Mg was shown in Table 2 like the case of an example 1.

[0011]

[Table 2]

No translation

[0012] Even if add Mg after dissolving nickel, Co, etc., and many ways whose melting points are more than Mg metals (659 degrees C) remain by the inside of an alloy, stripping to the outside of an alloy is controlled and it releases the inside of a furnace to atmospheric air at the time of a dissolution activity as Table 1 and Table 2 show, it turns out that it becomes possible to work safely more.

[0013]

[Effect of the Invention] Manufacture of a safer hydrogen storing metal alloy can be performed by making Mg content in an alloy into a predetermined thing by the manufacture approach of the hydrogen storing metal alloy of this invention, and controlling the evaporation at the time of the dissolution.

TECHNICAL FIELD

[Field of the Invention] Especially this invention relates to the manufacture approach of the hydrogen storing metal alloy for negative electrodes used for a nickel hydrogen rechargeable battery about the manufacture approach of a hydrogen storing metal alloy.

PRIOR ART

[Description of the Prior Art] In a nickel hydrogen rechargeable battery, the RF dissolution approach, the arc solution process, etc. have been used from the former as the dissolution approach of the hydrogen storing metal alloy used for a negative electrode. Moreover, rare earth metals, such as La, Ce, Pr, Nd, and Sm, and the metal of the misch metal (henceforth "Mm") which are those mixture, nickel, cobalt, manganese, and aluminum have been used for a raw material. By making magnesium contain about 0.5% of the weight in an alloy recently in addition to these metals has shown that pulverization is controlled or a hydrogen absorption total amount increases. Although Mg is contained in the conventional Mm etc. as an impurity, it evaporates during the dissolution and hardly remains in the alloy which went up by the ability doing. Since the melting point becomes low [the alloy of high things and rare earth, and Mg] as the reason compared with the metal of others [maximum vapor tension / of magnesium], it turns out that the dissolution becomes early, and the time amount which is in a molten metal as a result becomes long, and it evaporates during the dissolution. When an ambient atmosphere permutation chamber is released to atmospheric air after the dissolution and casting by adhering to a fusion furnace wall, the magnesium which evaporated has the possibility of combustion or explosion, and is very dangerous.

EFFECT OF THE INVENTION

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[Problem(s) to be Solved by the Invention] This invention solves the technical problem of these conventional technique, controls evaporation of the magnesium under dissolution, makes the magnesium of the specified quantity contain in an alloy, and offers the approach of securing the insurance when releasing the inside of a furnace to atmospheric air after vacuum melting or the ambient atmosphere dissolution.

MEANS

[Means for Solving the Problem] This invention is characterized by adding, after having the description in the melting point using Mg metal or Mg alloy 650 degrees C or more as a raw material for adding Mg and dissolving refractory metals, such as nickel and Co, further. Then, when the addition raw material of Mg adds the alloy which made the melting point 650 degrees C or more, or magnesium metal, the effectiveness that the amount of Mg in which the time amount in which the metal which magnesium contained exists as a molten metal evaporates from a molten metal by becoming short is controlled is expected by adding, after refractory metals, such as nickel and Co, fuse. As a result, the coating weight of Mg to a furnace wall etc. can decrease, and the magnesium content in the alloy which can advance an activity now to insurance by the time of atmospheric-air release, and was further done in the inside of a furnace can be made high.

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alloy for electrodes. For example, heat treatment can be performed at 800–1200 degrees C under inert atmospheres, such as Ar gas, (0.08–0.2MPa) for 5 to 20 hours, it can grind so that it may become the mean particle diameter of 4–70 micrometers under inert atmospheres, such as Ar, after that with an impact type, a grinding type grinder, or grinders, such as a jet mill, and the hydrogen storing metal alloy of this invention can be obtained.

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